

A SURVEY OF POTENTIAL POLLUTANTS
AND REGULATIONS ASSOCIATED
WITH GEOTHERMAL FACILITIES

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by
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INTRODUCTION

Though the use of geothermal energy to produce electricity began in 1904 in Lardello, Italy, it has only been within the last 15 years that significant progress has been made towards utilizing geothermal resources in the United States. To date, this development has been centered in the Geysers region of California, but known geothermal resource areas have been identified in Oregon, Nevada, Montana, Wyoming, Idaho and Hawaii and potential geothermal resources exist in many other states. Other areas of the world that have known geothermal resources include Japan, New Zealand, Indonesia, the Phillipines, Chile and Ecuador.

Geothermal resources have the potential to provide a source of relatively clean, safe and independent energy for certain areas of the world that possess the necessary geological attributes to permit the formation of geothermal reservoirs. Hawaii is one such area. Geothermal power development however is not without some potential problems. Certain emissions from geothermal facilities may constitute an environmental hazard. The formative state of the industry in the United States however, is reflected in the paucity of data available on health and environmental hazards specifically associated with geothermal power generation. Though recent exploitation of geothermal sources in California has produced a significant body of information on short term problems, little information exists regarding the long term effects of geothermal development.

The purpose of this document is to provide a non-technical summary of currently available information on potential pollutants which may be discharged from geothermal facilities in Hawaii, to provide an abstract of the properties of those substances and to identify and summarize regulations governing those substances in Hawaii as well as in other jurisdictions.

The emphasis in this discussion has been placed on those substances most likely to constitute a potential problem in emission from geothermal facilities in Hawaii. These tend to be emitted into the atmosphere and as such the primary focus here is on atmospheric emissions.

The report is organized into three parts. The first briefly introduces the reader to the nature of geothermal resources, the second discusses the type of emissions likely to be encountered that affect air quality and the third discusses the types of emissions likely to affect water quality.

GEOHERMAL POWER

Geothermal (literally meaning earth's heat) resources refers to heat sources within the earth from which useful energy can be extracted. Only naturally occurring bodies of steam and hot water have proved useful to date for this purpose, but bodies of hot rock may someday be economically feasible to use for energy production.

Geothermal resources in Hawaii are formed when groundwater is heated at depth by hot rock or magma and is trapped by a relatively impermeable cap rock. These caps may consist of basalt, sedimentary rock, weathered ash and dikes. The aquifer is charged by normal precipitation and perhaps sea water intrusion. Fumaroles associated with local volcanism provide a vivid example of naturally occurring geothermal emissions.

Exploitation of such resources consists of extracting the heated water or steam and using it to power a turbine which propels an electric generator. The geothermal fluids may be dry steam, hot water or a mixture of both. The Geysers region in California is a dry steam resource. These types of geothermal resources are generally cheaper and easier to utilize than the wetter geothermal systems that characterize those wells drilled to date in Hawaii.

Much of the data pertinent to Hawaii's geothermal resources comes from the Hawaii Geothermal Project's well A on the lower east rift of Kilauea volcano. The well, drilled to a depth of 6,435 feet (5,800 feet below sea level), yielded hot water of 600 degrees Fahrenheit which could be flashed to steam at a pressure of 60 to 70 pounds per square inch -- sufficient to power a turbine. The Hawaii Geothermal Project was both a research and demonstration project that evaluated the potential of the resource to provide commercially useable electricity.

The steam and water extracted from subterranean geothermal reservoirs include and are accompanied by various substances which may pose environmental and health problems. The degree to which they pose a problem depends on many factors including the toxicity of the substance under consideration, their rate of emission from the facility, abatement measures used, meteorological conditions in the immediate area and the physical nature of the emission process.

The substances emitted from a geothermal facility (in addition to steam and water) vary depending on the chemistry of the particular geothermal reservoir being tapped. The chemical constituents of the aquifer and the heat of the resource play an important role in determining the chemical composition of the fluids and dissolved solids that are emitted. In addition if sea water intrudes into the reservoir, the chemical composition of the geothermal fluids will derive in part from the chemistry of the sea water. Such intrusion of salt water into the Ghyben-Herzberg lens (a lens of fresh water which floats on salt water) may be due to the high temperatures of the underlying rock. Potentially toxic emissions may also derive from temperature induced reactions in organic sediments and from magmatic degassing. Periods of volcanic activity may increase the concentrations of certain emissions from a geothermal facility.

Physical Nature of the Emission Process. The physical nature of the emission process determines the dispersion and deposition of various substances into the atmosphere. Pollutants may be emitted as gases or vapors, material contained in drift droplets (suspended or in solution) and, possibly as dry particulates.

Several factors govern the physical nature of the emission process: the type of pollutant (gas or vapor or drift droplet), the release point location, the height, velocity and temperature of the release point, the initial interaction between the plume of emissions and the release point and the size distribution and mass of the drift droplets.

Examples of some of the interactions that must be described to adequately predict ambient levels of pollutants include measurement of the dilution with ambient air that occurs after a substance is released from a facility, the size of the drift droplets in the emission plume (which governs their velocity and is determined by coalescence of droplets, evaporation and condensation), and atmospheric temperatures relative to temperatures of the gaseous emissions (warm emissions into a cooler atmosphere will tend to rise further and ambient levels of a substance measured at ground level in the immediate vicinity will thus tend to be lower).

Meteorology. Once the plume of emissions enters the atmosphere, its dispersion and subsequent deposition is governed by meteorological conditions in the area under consideration. Wind velocity and directions, temperature, precipitation, topography all play an important role in the process.

Air Quality Standards. Air quality standards have been developed for many potential and known atmospheric pollutants throughout the United States. These standards govern rates of emissions per unit time, ambient air, occupational air quality, concentrations of substances averaged over various periods and occasionally amounts of emissions per various other units such as kilowatt hours.

Ambient Air Standards. The Environmental Protection Agency defines ambient air as "that portion of the atmosphere, external to buildings, to which the general public has access." Ambient air standards are issued to protect the public health and welfare and are usually expressed as concentrations of a substance averaged over a given unit of time. Such standards may specify 1 hour, 24 hour or annual averaging periods as well as ceiling values which pollutant concentrations are never supposed to exceed.

Nationally, the Environmental Protection Agency has the responsibility for regulating air quality. They have developed a set of National Primary Air Standards and Secondary Air Standards. Primary Air Standards are intended to define a level of air quality that is necessary to protect the public health with an adequate margin of safety. Secondary Air Standards define levels of air quality which are believed necessary to protect the public welfare from any known or anticipated adverse effects of a pollutant.

The Environmental Protection Agency also issues new source performance standards regulating the emissions of certain substances from new emission sources. It also regulates new and existing sources to insure that emission levels are maintained for certain substances so as to prevent significant deterioration in air quality.

In Hawaii ambient air standards are set by the Department of Health.

Emission Rates. Because ambient concentrations of controlled pollutants are influenced by many factors other than the absolute volume of emissions from a source, many jurisdictions also regulate the rate and volume of emissions of certain substances. These may be expressed in pounds per day, tons per day or tons per year as well as other units such as pounds per kilowatt hour.

Occupational Air Quality. Various toxic and potentially toxic substances are controlled so as to minimize health hazards they pose to workers. On the national level the National Institute of Occupational Safety and Health of the Center for Disease Control, Public Health Service, develops standards and criteria for standards for many potentially deleterious substances likely to

to be encountered in a work environment. The Occupational Safety and Health Administration has the regulatory authority to implement safety and health standards. The American Conference of Governmental Industrial Hygienists (ACGIH) also develops standards for worker exposure to certain substances that are considered authoritative. ACGIH defines three categories of airborne concentrations of substances that are believed to represent conditions to which workers may be exposed without adverse affect for specified periods of time. These are:

Threshold Limit Value-Time Weighted Average (TLV-TWA)

The time weighted average concentration for a normal 8 hour workday or 40 hour workweek, to which nearly all workers may be repeatedly exposed, day after day, without adverse effect.

Threshold Limit Value-Short Term Exposure Limit (TLV-STEL)

The maximal concentration to which workers can be exposed for a period up to 15 minutes continuously without suffering from: 1) irritation, 2) chronic or irreversible tissue change, or 3) narcosis of sufficient degree to increase accident proneness, impair self rescue, or materially reduce work efficiency, provided that no more than four excursions per day are permitted, with at least 60 minutes between exposure periods, and provided that the daily TLV-TWA also is not exceeded. The STEL should be considered a maximal allowable concentration, or absolute ceiling, not to be exceeded at any time during the 15-minute excursion period.

Threshold Limit Value-Ceiling (TLV-C)

The concentration that should not be exceeded even instantaneously.

Standards promulgated for concentrations of substances in the workplace environment are invariably less stringent than those generated for ambient air.

Modeling. In order to predict the effects of geothermal emissions on air quality for a particular substance or substances in a region, various modeling techniques are sometimes used. These techniques can assist in determining the appropriate abatement measures necessary to maintain a given ambient air quality standard. Modeling techniques attempt to represent the complex and diverse physical, chemical and meteorological processes which interact to determine ambient air concentrations of a substance at defined locations relative to the

emission point. Regional models may attempt to predict ambient concentrations of a pollutant over a hundred miles from an emission point (or points) while microscale models may attempt to assess air quality at distances of 10 meters from a source.

The complexity of the data required by a given model is a function of the sophistication of the model. All models however, require some meteorological data, as well as data on the emission process such as that outlined above, topography, the physical and chemical nature of the substance being investigated, and emission rates. Interpretation of the model also requires detailed information on the ambient air quality of the area without the contribution of the emission source under study. In the case of geothermal facilities in Hawaii where volcanic and fumerolic emissions occur naturally, a thorough characterization of the distribution of these sources and their emissions would be essential to accurate application of some models.

SPECIFIC DATA ON POTENTIAL POLLUTANTS

HYDROGEN SULFIDE

One of the most common constituents of geothermal emissions is hydrogen sulfide (H_2S) a colorless gas with the characteristic odor of rotten eggs. Hydrogen sulfide occurs naturally in volcanic gases, coal, natural gas and oil. It may also be produced in swamps, cesspools and sewers as a result of the anaerobic decomposition of organic sulfur bearing materials. In volcanic gases, H_2S is thought to derive from the action of steam on inorganic sulfides at high temperatures. In industrial processes, hydrogen sulfide is produced as a by-product of removing sulfur from fossil fuels and in the production of coke, heavy water for atomic reactors and kraft paper. In some cases, hydrogen sulfide by-products from these processes are reclaimed by conversion to sulfur or sulfuric acid and then sold.

Hydrogen sulfide was recognized as a toxic substance as early as the 18th century when various ill effects and fatalities noted among sewer workers and cesspool and privy cleaners were correlated with the gas. Experimental assessments of the effects of hydrogen sulfide during the 19th century demonstrated its irritant properties and its ability to produce respiratory distress and death in sufficient concentrations.

Hydrogen sulfide is detectable by humans at concentrations as low as 12 parts per billion (ppb). As such, it provides a distinct warning of its presence at concentrations far below those that are considered hazardous. At higher concentrations, however, (greater than 150 parts per million), it exerts a paralyzing effect on the human sense of smell thereby depriving an exposed individual of adequate warning.

At high concentrations hydrogen sulfide has a physiological effect similar to and nearly as toxic as hydrogen cyanide. Human symptoms vary with the concentration of the gas and the duration of exposure. The ill effects of hydrogen sulfide exposure have been frequently characterized as chronic, sub-acute and acute. The sub-committee on hydrogen sulfide of the National Research Council, National Academy of Sciences offers the following categorization:

Acute Intoxication

Effects of a single exposure to massive concentration of hydrogen sulfide that rapidly produce signs of respiratory distress. Concentrations approximating 1,400 ug/liter (1000 part per million [ppm]) are usually required to cause acute intoxication.

Sub-Acute Intoxication

Effects of continuous exposure to mid-level (140 to 1,400 ug/liter [100 to 1,000 ppm]) concentrations of hydrogen sulfide. Eye irritation (gas-eye) is the most commonly reported effect, but pulmonary edema (in the absence of acute intoxication) has also been reported.

Chronic Intoxication

Effects of intermitten exposures to low to intermediate concentrations (70 to 140 ug/liter [50 to 100 ppm]) of hydrogen sulfide, characterized by "lingering", largely subjective manifestations of illness.

(National Research Council 1978:97)

In acute intoxication, hydrogen sulfide poisoning is systemic in nature and its toxic effects are believed to result from the inhibition of aerobic metabolism. Experimental exposure of men to hydrogen sulfide in various concentrations during the early part of this century clearly demonstrated that concentrations of 500 ppm or greater poses a serious and immediate threat to life. At higher concentrations, (500-1000 ppm) it may cause permanent effects on the central nervous system. At this level, rapid breathing is induced which leads to depletion of carbon dioxide in the blood stream (the presence of CO₂ serves to trigger respiration). If this progresses far enough respiration ceases and asphyxiation may result. At about 1500 ppm and above the result is more intense and at about 2000 ppm the victim succumbs within one or two breaths. At this level respiratory failure is the result of direct paralysis of the respiratory center by hydrogen sulfide.

Acute intoxication most frequently occurs in industrial situations where hydrogen sulfide is either used directly or is a by-product of a manufacturing process.

Sub-acute hydrogen sulfide poisoning also occurs most frequently in industrial circumstances where workers are exposed either to low concentrations of H_2S for long periods or higher concentrations for shorter periods. Sub-acute poisoning is characterized by the irritative effect hydrogen sulfide has on the moist membranes of the eye and respiratory tract. Inflammation of the conjunctival and corneal tissues of the eye can appear after exposure to H_2S concentrations of 50 ppm for approximately 1 hour. Hydrogen sulfide has a slight anesthetic effect on the eye and, as such, pain is not always immediately present. Subsequently however, acute conjunctivitis (inflammation of the mucous membrane covering the eye and eyelid lining) may develop with characteristic symptoms including pain, excessive tearing, blurred vision, and photophobia. More severe forms may develop corneal ulceration and scar formation with permanent visual impairment. All of the mucous membranes of the respiratory tract appear to be easily irritated by hydrogen sulfide. Bronchitis, laryngitis, rhinitis and pharyngitis may also develop.

There is no clear agreement among researchers that chronic hydrogen sulfide poisoning is a definable pathologic entity. Repeated or prolonged exposures to low levels of H_2S are thought by some to produce generalized symptoms of fatigue, loss of memory and an ill defined malaise. Empirical verification of such chronic symptoms however is lacking. Systemically, hydrogen sulfide exerts its effects only in the form of a free unoxidized gas in the bloodstream. Hydrogen sulfide however is rapidly oxidized in the blood and its effects are considered non-cumulative.

Effects on vegetation and wildlife. Though a significant number of experiments designed to define the effects of hydrogen sulfide on plants and animals have been conducted, the intent and methodology of the experiments vary so widely as to make any general conclusions tentative at best.

In animals, early experimenters were interested in determining the physiological mechanisms of hydrogen sulfide poisoning. As a result, the data gathered tended to result from exposure of experimental animals to relatively high concentrations of H_2S -- much higher than would normally be expected from occupational or ambient exposures. Experiments with aquatic organisms indicate that effects vary widely with the pH and temperature of

the water, the specific organism and its maturity.

Observations of H_2S effects on plants show a very wide range of susceptibility. However, long term exposure to concentrations below .03 ppm appears to be harmless and in some species deprived of sulfur in their nutrients, actually appeared to stimulate growth.

In terms of the effects of H_2S on plants near planned geothermal developments on the island of Hawaii, little can be said with certainty. The complex of endemic plants that are present in the area may have developed a higher tolerance for ambient hydrogen sulfide than plants that are native to areas without active volcanism. In general, the effects of H_2S on plants and animals at low concentrations likely to be encountered near a geothermal facility is unclear. Both the physical and biochemical processes involved are not clearly understood and species specific empirical data are lacking.

Hydrogen Sulfide As A Nuisance Odor. In addition to considerations of direct health related consequences of exposure to hydrogen sulfide, the impact of H_2S as a serious nuisance odor must be considered. As mentioned, hydrogen sulfide has the characteristic odor of rotten eggs; a smell that is distinctly unpleasant to the majority of the population. As mentioned above, H_2S has been detected by humans at a level as low as 12 ppb. Though sensitivity, tolerance and habituation to hydrogen sulfide vary from individual to individual, the threshold at which most people would consider it a nuisance and an objectionable pollutant is likely to be far below that at which it has been demonstrated to be a health hazard. For example, the California Air Resources Board set the ambient air quality standard for H_2S in California at .03 ppm averaged over 1 hour. This resulted from a recommendation from the State Department of Health based on an experiment in which the threshold concentration for the detection of hydrogen sulfide based on its odor was measured for 16 people. The range in this experiment was from .012 to .069 ppm. The mean was .029 ppm. The standard set is intended to minimize the nuisance potential of hydrogen sulfide. It is not intended to insure that people will not detect its odor, particularly since short term concentrations may exceed .03 ppm. Studies have not been able to detect any health effects

at this low a concentration.

Considerable debate still exists over the appropriateness of this standard. Many people can detect the odor below this concentration and only brief exposure to do so is required. The California standard however uses a one hour averaging time to measure the concentration. Some have urged a shorter averaging time and/or a lower concentration. On the other hand, no physical ill effects have been demonstrated at concentrations this low. Occupational standards allow prolonged exposure to levels as high as 20 ppm and no clear deleterious effects to health have been detected at concentrations as great as 100 times the California standard. As a result others argue that the standard is set too low and the averaging times and/or the concentrations should be increased.

Other Environmental Effects. Other consequences of atmospheric emissions of hydrogen sulfide include its potential to tarnish brass and silver and the fact that it can discolor certain lead based paints. Hydrogen sulfide also reacts in the atmosphere to form sulfur dioxide (SO_2). This varies as a function of temperature, humidity and other constituents of the atmosphere.

Hydrogen Sulfide Abatement Techniques

Because hydrogen sulfide is of particular concern at low concentrations due to its nuisance odor and because of its toxicity at higher concentrations, abatement measures designed to reduce hydrogen sulfide emissions have been applied to geothermal facilities. Again, California has taken the lead in stimulating development of such abatement measures because of the low ambient concentration standard they have adopted and because of the geothermal development at the Geysers area. The type of emission abatement measures adopted is dependent on the rate of emissions and the ambient level that must be maintained.

There are currently two types of abatement techniques employed at the Geysers: the iron catalyst peroxide caustic system (ICPC) and the Stretford peroxide surface condensor (SPSC). Both of these are "down stream" systems designed to control off gas after it has passed through the turbine.

The ICPC uses ferrous sulfate added to the cooling water to oxidize hydrogen sulfide into sulfur and insoluble ferrous sulfate. A caustic is used to scrub hydrogen sulfide in gases back into solution and peroxide is used to regenerate the iron catalyst. The disadvantages of the system are that it presents a corrosion problem, chemical costs are high and the wastes produced must be disposed of carefully. The ICPC system can theoretically attain a 90% efficiency in reducing hydrogen sulfide emissions though in practice this has been difficult to maintain.

The SPSC system also controls H_2S off gases by absorbing them in an alkaline solution (e.g., sodium bicarbonate) which is then oxidized to sodium bicarbonate and sodium vanadium trioxide. Theoretically, the Stretford process can achieve 99% efficiency. The elemental sulfur produced can be sold to recover some costs but chemical costs with this system are high.

Research on new abatement technology continues. Some of the new techniques include upstream processes which remove hydrogen sulfide before

the fluids reach the turbine. This has the advantage of reducing corrosion problems and reducing emissions even if the generator/turbine have to be shut down and the fluids vented as a result.

The Cuprosol (trade name) process reacts hydrogen sulfide with copper sulfate to produce copper sulfides which are then oxidized to copper sulfate in a regenerator. Pilot studies indicate that this process reduces corrosion and chemical costs below that of the ICPC process. Theoretical efficiency may be as high as 99.9% reduction of H_2S .

A second up-stream process removes H_2S by recondensing steam prior to its use at the turbine, removing non-condensable gases (including hydrogen sulfide) and then re-evaporating the steam to power the turbine. It purportedly removes all non-condensable gases at a rate exceeding 90% and can be used at both liquid and dry geothermal sources. The condensate produced is then discarded.

A third experimental process is designed to be used in conjunction with other down stream abatement measures. The 'steam stripping' process removes hydrogen sulfide dissolved in water by "stripping" it from condensate by channelling waste steam through it. The gaseous hydrogen sulfide can then be removed by other methods. The advantage of this technique is that it reduces the cost of treating the condensate.

Governmental Regulations and Air Quality Standards

Because the nuisance odor of hydrogen sulfide is detectable at such low levels, substantial effort has gone into regulating geothermal power plant emissions in California. Much of the following data is taken from regulations established there since they are the most thorough and stringent. Examples of standards from other areas are summarized in tabular form at the end of this section.

To give some idea as to the volume of hydrogen sulfide emitted from some operating power plants in the Geysers area Table 1 is presented.

TABLE 1

GEYSERS STEAM FIELD STATISTICS

(From Environmental Impact Report for Union Oil Geothermal Division L'Esperance Leasehold, Lake County, Ecoview Environmental Consultants, 1980)

Unit No. (MW load)	Potential MW/yr (1)	1979 Actual MW/yr (2)	1979 lbs. steam used	1979 Klb/MW	1979 (H ₂ S) (3)	Potential tons H ₂ S (4)	Emission Factor (5)	1979 Calculated tons H ₂ S (6)
1. (12MW/hr)	105,120	61/370	1,481x10 ⁶	24.132	204	151	100%	151
2. (14MW/hr)	122,640	41,220/ 5,740	1,731x10 ⁶	24.304	165	142/12	50%	136
3. (27.5MW/hr)	240,900	117,651	2,905x10 ⁶	24.691	494	689	8%	55
4. (24.5MW/hr)	240,900	87,620	1,986x10 ⁶	22.666	389	386	6%	23
5. (55MW/hr)	481,800	359,300	6,978x10 ⁶	19.421	300	1047	7%	73
6. (55MW/hr)	481,800	340,300	6,799x10 ⁶	19.979	355	1209	9%	109
7. (55MW/hr)	481,800	374,400	6,916x10 ⁶	18.492	244	775	100%	775
8. (55MW/hr)	481,800	362,900/ 39,420	7,044.10 ⁶	19.410	124	439/47	100%/50%	414
9. (55MW/hr)	481,800	415,800/ 41,340	8,096x10 ⁶	19.263	52	211/21	100%/50%	201
10. (55MW/hr)	481,800	392,400/ 35,880	7,930x10 ⁶	20.208	62	246/23	100%/50%	235
11. (110MW/hr)	963,600	546,500	11,253x10 ⁶	20.591	358	2014	6%	121
12. (110MW/hr)	963,600	740,250	14,156x10 ⁶	18.969	86	609	15%	91
13. (62MW/hr)	543,120	173,400	3,386x10 ⁶	19.509	156	264	35%	92

(1) Potential megawatts/year - Does not take into account downtime scheduled for maintenance, overhauls, tests, etc.

(2) Actual MW/yr - On units 2,8,9,10 this statistic in the lower level reflects load generated during the 1979 interim abatement period.

(3) (H₂S) - In P.P.M. (10). This is a 12 month average of test results from incoming steam at each unit.

(4) Potential tons H₂S - Subscript data on units 2,8,9,10 reflect amounts of H₂S emitted during abatement periods. Superscript data reflects total possible, given 1979 steam data.

(5) Emission Factor - Units 1 and 7 are unabated therefore 100%
Units 2,8,9,10 are 100% during unabated periods and assume 50% during abatement period as they use only Fe+ catalyst
Units 3,4,5,6,11,12 are assigned emission factors based on source test data received.

(6) Calculated tons H₂S - is arrived at by multiplying emission factor x potential tons H₂S. In the case of units 2,8,9,10, one must multiply the subscript emission factor times the subscript potential tons H₂S, then subtract that amount from the superscript data.

National Regulations

There are no primary or secondary air quality standards for hydrogen sulfide at the national level. The Environmental Protection Agency does require permits from H_2S sources that emit more than 10 tons per year to prevent significant deterioration of air quality (40 CFR 52.21). EPA does not define standards of performance for new stationary sources for geothermal facilities. Kraft paper mills, which also emit H_2S in quantity, are limited to an emission concentration of 5 ppm total reduced sulfur by volume on a dry basis (40 CFR 60). Total reduced sulfur in this context is defined as the "sum of the sulfur compounds H_2S , methyl mereaptan, dimethyl sulfide and dimethyl sulfate.

Hawaii has no ambient air standard for hydrogen sulfide nor any emission rate regulations.

California has developed a stringent set of regulations to control hydrogen sulfide emissions from geothermal plants. As stated earlier, the California ambient standard was set at .03 ppm or 30 parts per billion.

California is divided into a number of air pollution control districts that set their own specific implementing regulations. Some of these are more stringent than others. The following discussion is taken from the regulations of the Lake County Air Pollution Control District (Lake County), the North Coast Air Basis (Del Norte, Humboldt, Trinity, Mendocino and Sonoma Counties) and the Imperial City Air Pollution Control District (Imperial County).

Each of the above jurisdictions relies on conditions attached to "Authority to Construct" permits. Such permits completely specify maximum emission rates, conditions under which these rates apply, the degree to which abatement is required. Lake County APCD sets out a detailed schedule for such emissions for scheduled and unscheduled power plant outages for various types of plants.

TABLE 2
SCHEDULED POWER PLANT OUTAGES
(Standards Given in % full flow H₂S)

TYPE OF FACILITY	ELAPSED TIME OF OUTAGE IN MINUTES				
	Outages Less Than 360 Minutes		Outages Greater Than 360 Minutes		
	Elapsed time 15 min.	360	15	90	240
Dual units with one unit operative	10% ^a within 15 min.		10% ^a within 15 min. and until start-up is initiated		
Single units capable of shunting 35% of full steam flow	35% ^a within 15 min.	Back on line or H ₂ S reduced to 10% of full unabated H ₂ S steam flow until start-up is initiated	35% ^a within 15 min.		10% within 240 min. and until start-up is initiated
Single units without the capability to shunt 35% of full steam flow	35% within 15 min.		35% ^a within 15 min.		10% within 90 min. and until start-up is initiated
Dual units with both units down simultaneously and capable of shunting 35% of full steam flow	40% ^a within 15 min.		40% ^a within 15 min.		10% within 240 min. and until start-up is initiated
Dual units with both units down simultaneously and no capability to shunt steam	40% ^a within 15 min.		40% ^a within 15 min.		10% within 90 min. and until start-up is initiated

^aThe necessity for occasional venting in excess of limits specified under an upset in coordinating well throttling and power plant start-up or shut down is acknowledged (refer to Article II, Section 510 of LCAPCD Rules and Regulations).

(From Lake County Air Pollution Control District Rules and Regulations, April 1981).

TABLE 3

UNSCHEDULED POWER PLANT OUTAGES
(Standards Given in % full flow H₂S)

TYPE OF FACILITY	ELAPSED TIME IN MINUTES				DECISION AS ENTERED IN LONG IS LESS THAN 420 MIN.		NO DECISION OR DECISION AS ENTERED INTO LOG IS GREATER THAN 420 MIN.	
	15	30	60	90	90	420	150	300
ual units with one unit perative	90%	50%	35%	10%	10%	continued	10% continued as at 90 min. until start-up is initiated	
ingle units capable of hunting 35% of full steam low	90%	50%	35%	Enter into log expected duration of outage	35%	Back on line or H ₂ S reduced to	10% within 150 min. and until start-up is initiated	
ingle units without the apability to shunt 35% f full steam flow	90%	50%	35%		as at 60 min.	10% of full unabated	10% within 150 min. and until start-up is initiated	
ual units with both units own simultaneously and apable of shunting 35% f full steam flow	90%	50%	40%		until start-up initiated	H ₂ S steam flow rate until start-up initiated	Continue at 60 min. unabated H ₂ S steam flow rate	10% within 300 min. & until start- up is initiated
ual units with both units own simultaneously and no apability to shunt steam	90%	50%	40%				10% within 150 min. and until start-up initiated	

The necessity for occasional venting in excess of limits specified under an upset in coordinating well throttling and power plant start-up or shut down is acknowledge (refer to Article II, Section 510 of LCAPCD Rules and Regulations).

From Lake County Air Pollution Control District Rules and Regulations, April 1981).

Effective January 1, 1985 H₂S emissions for Lake County APCD unscheduled or scheduled, for all types of facilities must be reduced to 10% of the full, unabated steam flow within 15 minutes of a power plant outage.

Lake County APCD also sets stringent emission rates.

1. All geothermal power plants for which an Authority to Construct permit is initially issued before January 1, 1981 shall emit no more than 175 grams of hydrogen sulfide per gross megawatt hour.
2. All geothermal power plants for which an Authority to Construct permit is initially issued on or after January 1, 1981 shall emit no more than 50 grams of hydrogen sulfide per gross megawatt hour.
3. All geothermal power plants shall, by January 1, 1991, emit no more than 50 grams of hydrogen sulfide per gross megawatt hour. However, this rule shall be subject to confirmation at a properly noticed public hearing to be held in 1987.

The following is excerpted from the Rules and Regulations of the Lake County Air Pollution Control District (as of April 28, 1981).

PERMITS

Article I Authority to Construct

Section 600 A written Authority to Construct shall be required to construct, erect, alter, or replace any equipment which may cause, potentially cause, reduce, control or eliminate the issuance of air contaminants. A single Authority to Construct may be issued for all components of an integrated system or process. Plans and specifications drawn in accordance with acceptable engineering practices shall be required before issuance of an Authority to Construct.

Section 601 An Authority to Construct shall be valid for a period of one (1) year from the date of issuance, or until a Permit to Operate is required, whichever occurs first. An Authority to Construct may be renewed annually for a maximum period of four (4) years. Any Authority to Construct permit or Determination of Compliance for a geothermal project for which construction has been initiated prior to the fourth annual renewal, may be renewed annually until such time as a Permit to Operate is issued for the project.

Section 602 The Air Pollution Control Officer shall deny an Authority to Construct for any new stationary source or modification of an existing source specified in subparagraph A of this section unless he determines that the emissions from the new source or modification may not be expected to result in the violation or measurable contribution to the continued violation of any

local, state or national ambient air quality standard and provided that the best available control technology as defined, will be used on the contaminant emitting equipment.

- A. The Air Pollution Control Officer shall apply the provisions of this section to:
 - 1. Any proposed new stationary source described in the application for the Authority to Construct which he estimates will emit:
 - a. More than either twenty (20) pounds per hour or one hundred fifty (150) pounds per day of nitrogen oxides, organic gases or any air contaminant for which there is a local, state or national ambient air quality standard, except carbon monoxide, or
 - b. More than either 150 pounds per hour or 1500 pounds per day of carbon monoxide.
 - 2. Any proposed modification of an existing stationary source described in the application for the Authority to Construct that he estimates will emit after modification:
 - a. More than either twenty (20) pounds per hour or one hundred fifty (150) pounds per day of nitrogen oxides, organic gases or any air contaminant for which there is a local, state or national ambient air quality standard, except carbon monoxide, or
 - b. More than either one hundred fifty (150) pounds per hour or 1500 pounds per day of carbon monoxide.
- B. The Air Pollution Control Officer may exempt from the provisions of this section any new stationary source or modification which he determines:
 - 1. Is a modification which eliminates, reduces, or controls air contaminant emissions from an existing source, provided that the emissions of any contaminant from the modified source will not be greater than such emissions were from the existing source, or
 - 2. Will be an addition to, or replacement for, an existing stationary source and will not result in emissions of any air contaminant greater than those from the existing source, or
 - 3. Will have demonstrable basin-wide air quality benefits. Calculations and technical data used by the Air Pollution Control Officer as the basis for granting the exemption shall be made to the Air Resources Board and Environmental Protection Agency, or

4. Will be used exclusively for providing essential public services, including but not limited to hospitals, police, and fire fighting facilities, and will employ the best practicable emission control methods and equipment.

Section 602.1 The Air Pollution Control Officer shall deny an Authority to Construct for a new source or a modification of an existing source specified in Section 600 unless he determines that the existing source or modification will operate within all applicable rules and regulations pertaining to the emission of air contaminants.

Section 603 When the Air Pollution Control Officer intends to grant an exemption under subparagraph B of Section 602, he shall publish a notice by prominent advertisement in at least one newspaper of general circulation in the District, and he shall notify in writing the U.S. Environmental Protection Agency and the California Air Resources Board of his intention. No exemption shall be granted until at least thirty (30) days after the date of publication and notification to the above agencies. In making his decision, the Air Pollution Control Officer shall consider any comments received, and in the case of exemptions proposed under paragraph B(3) of Section 602, a condition of a decision to grant an exemption shall be at the concurrence of the California Air Resources Board and the U.S. Environmental Protection Agency. In the absence of written notice by the Air Resources Board or the Environmental Protection Agency within thirty (30) days from the date of publication, the Air Pollution Control Officer may assume their respective concurrence.

Section 604 Notwithstanding the criteria specified in paragraph A of Section 602, the Air Pollution Control Officer may apply the provisions of this Article to any new or modified stationary source if, in his opinion, the emissions from the source might result in a violation or a measurable contribution to the continued violation of any local, state, or national ambient air quality standard.

Section 605 Before granting or denying an Authority to Construct for any new stationary source or modification subject to the provisions of this Article, the Air Pollution Control Officer shall:

- A. Require the applicant to submit information sufficient to describe the nature and amount of emissions, location, design, construction, and operation of the source; and to submit any additional information necessary to make the analysis required by this Article.
- B. Require the applicant to submit any projected expansion plans for the stationary source described in the application for the Authority to Construct for the ten (10) year period subsequent to the date of application for the Authority to Construct.
- C. Analyze the effect of the new stationary source or modification on air quality. Such analysis shall consider expected air contaminant emissions and air quality in the vicinity of the new source or modification within the Air Basin and within adjoining air basins at the time the source or modification is proposed to commence operation. Such analysis shall be based on application of existing state and local control strategies.

- D. Make available for public inspection at the District office the information submitted by applicant, the Air Pollution Control Officer's analysis of the effect of the source on air quality and the preliminary decision to grant or deny the Authority to Construct. This will include all relevant information except that protected as a trade secret.
- E. Publish a notice pursuant to Section 6061 of the Government Code in a newspaper of general circulation in the District stating where the public may inspect the information required in Section 605 (D). The public shall have thirty (30) days beginning on the date of publication to submit their comments. Copies of this notice should be forwarded to the U.S. Environmental Protection Agency, the California Air Resources Board and all adjoining air pollution control officers in other air basins.
- F. Consider the public comments submitted.

Section 605.1 Geothermal Wells: If after review of the ten-year expansion plan required under Section 605 (B), the Air Pollution Control Officer determines that existing air pollution abatement technology is not sufficient to allow the plan to be implemented in accordance with Sections 602 and 602.1, he shall limit the geothermal project to no more than the first three (3) geothermal exploratory wells each capable of producing 90,000 pounds of steam per hour at free flow of any quality or after the first three (3) geothermal exploratory wells are drilled, cause the cessation of drilling when the cumulative capability of all wells drilled as part of the exploratory project is 350,000 pounds of steam per hour. Additionally, exploratory projects shall not be allowed under this section if they could be expected by the Air Pollution Control Officer to be utilized by a proposed electric power plant for which any application or notice has been filed with the California Energy Resources Conservation and Development Commission. Permits for subsequent wells capable of being part of the same geothermal project shall not be issued until such time as abatement technology sufficient to allow the ten-year expansion plan to be implemented in compliance with Sections 602 and 602.1 is demonstrated.

Section 606 Receipt of an Authority to Construct shall not relieve the owner or operator of responsibility to comply with any applicable local, state or national air pollution rules or regulations.

Section 607 Any Authority to Construct granted pursuant to this Article shall be forwarded to the California Air Resources Board within thirty (30) days of issuance, together with the data used by the Air Pollution Control Officer in the air impact assessment process to allow review thereof by the Air Resources Board pursuant to its authority under the Health & Safety Code to review air pollution control district enforcement procedures and actions. In the absence of written notice of nonconcurrence by the Air Resources Board within thirty (30) days from the date of receipt by the Air Resources Board, the Air Pollution Control Officer may assume its concurrence.

Section 608 Notwithstanding Sections 602, 604, and 605 (C) of the District's rules, the Air Pollution Control Officer shall issue an Authority to Construct or other required documents to any geothermal power plant development project (power plants, production wells, and geothermal fluid transmission lines),

which meets the following prescriptive criteria and utilizes the best available control technology.

1. Power plants and geothermal fluid transmission lines must limit on a continuous basis the hydrogen sulfide emission rate to no more than five (5.0) pounds per hour (2.3 kilograms per hour) per one million (1,000,000) pounds per hour of steam flow received;
2. The proposed power plant must be located such that not more than one permitted geothermal power plant (within the District) is closer than 0.6 mile, and no populated areas (as defined in Chapter 21 of the Lake County Code, Article XXV, Section 21-73.6a(1)) are within 1.0 mile of the proposed location;
3. Geothermal development wells must limit the hydrogen sulfide emission rate on a continuous basis during air drilling, clean-out, initial testing and reworking to no more than five (5.0) pounds per hour (2.3 kilograms per hour);
4. Wells on stand-by vent shall be located no closer than 0.5 mile from a populated area (as defined in Chapter 21 of the Lake County Code, Article XXV, Section 21-73.6a(1)), and emissions shall be no greater than an average of one (1) pound per hour per well based on the number of completed wells for the associated power plant's steamfield;
5. In the judgment of the Air Pollution Control Officer, the facility must be able to readily show compliance with all other rules and regulations limiting emissions of emittants other than hydrogen sulfide; and
6. No individual property owner or legal resident within a one-mile radius of the proposed power plant site or 0.5 mile from an associated drilling pad makes a request for a New Source Review of the project under Chapter IV, Article I of the Lake County Air Pollution Control District Rules and Regulations.

The Lake County Air Pollution Control District shall make proper public notice and reasonable attempts to notify affected parties (in writing) of the intent to issue permits under Rule 608, thirty (30) days prior to such permits being issued. The notice shall include a statement that affected parties may request a detailed New Source Review of the proposed power plant. Permit issuance after the 30 days notice pursuant to this rule shall be final.

Ambient Air Quality Standards for H₂S in Other Areas. Though California has led the way in development of H₂S regulations, other states and nations have also established criteria. Examples of some of the short term standards follow:

Jurisdiction	Standards mg/m ³	ppm	Measurement Averaged Over	Comments
California	.042	.03	1 hour	
Minnesota	.042	.03	30 minutes	Not to be exceeded more than twice in 5 consecutive days
Montana	.042	.03	30 minutes	
New Mexico	.0042	.003	30 minutes	
New York	.014	.01	30 minutes	
Pennsylvania	.1	.072	1 hour	
Texas	.112	.08	30 minutes	Residential areas
Texas	.168	.12	30 minutes	Industrial areas
Bulgaria	.008	.006	20 minutes	
West Germany	.3	.2	30 minutes	
East Germany	.013	.009	30 minutes	
Finland	.15	.1	30 minutes	
Israel	.15	.1	30 minutes	
Italy	.1	.07	30 minutes	
U.S.S.R.	.008	.006	30 minutes	

Emission concentrations standards also vary widely:

New Mexico Natural Gas Plants	10 ppm
Alabama	150 ppm
Texas Refinery (Start Up/Shut Down)	.3 ppm
West Germany Coke Oven Off Gas	1000 ppm
Sweden	6.5 ppm

Occupational Exposure Regulations

O.S.H.A. standards for worker exposure specify an acceptable ceiling concentration for worker exposure of 20 ppm which should not be exceeded during an 8 hour shift. However, they also specify a second acceptable maximum peak above the acceptable ceiling of 50 ppm. O.S.H.A. allows worker exposure to above 20 ppm and below 50 ppm for 10 minutes only once during an 8 hour day provided no other excursion into these levels occurs. (29 CFR 1900.1000)

The National Institute of Occupational Safety and Health (NIOSH) has recommended a more stringent standard of 10 ppm/15 mg/m³ which is designed to protect the health and provide employee safety for 10 hour work days/ 40 hour work weeks over a working lifetime. They also recommend standard sampling and analysis methods, medical surveillance of employees, standard labeling and posting of warnings, protective devices to be used in emergencies, work practices, and record keeping standards (NIOSH, 1977).

The American Conference of Governmental Industrial Hygienists recommends a threshold limit value-time weighted average of 10 ppm. They have also set a tentative short term exposure limit of 15 ppm.

Hawaii Occupational Safety and Health Standards specify a TLV-TWA (8 hours) for H₂S of 10 ppm and a short term exposure limit of 20 ppm for 5 minutes.

It should be noted that all of these occupational exposure criteria were not developed for the population at large and extrapolation of these levels to situations and exposures characteristic of ambient air to which the general populace is continually exposed is inappropriate.

Monitoring Techniques

To ensure replicability and precision, jurisdictions that regulate a substance commonly specify air sampling methods and analytical method to measure the substance under consideration. In addition continuous monitoring devices are also sometimes specified.

For example, California's specified analytical technique for determining H₂S concentrations is the cadmium hydroxide stractan colorimetric method. In this technique a measured volume of air is passed through an alkaline suspension of cadmium hydroxide. The sulfide is precipitated as cadmium sulfide to prevent oxidation of the sulfide by air. The sulfide is then reacted with N, N-dimethyl-p-phenylenediamine and ferric chloride to yield methylene blue. The intensity of the methylene blue color is proportional to the amount of sulfide present in the sample. This method, though not

readily used in the field, is used by the California Air Resources Board and the California Air and Industrial Hygiene Laboratory to calibrate other detectors. The technique has been estimated to be accurate to within $\pm 10\%$ when measuring H_2S in the 10 to 30 ppb range.

Other detection methods include:

Flame photometric detectors which measure the specific spectral adsorption of an atomized sample. To measure H_2S these detectors must be equipped with scrubbers to separate hydrogen sulfide from sulfur dioxide. Though potentially quite accurate the system requires frequent calibration and verification of H_2S transmission due to problems associated with the scrubber system.

Gas chromatographs which separate the H_2S from other compounds and determines its concentration through differential adsorption, may also be used. Though complex and requiring constant maintainance, Pacific Gas and Electric has used these devices with success in the Geysers region of California. When properly maintained and operated their sensitivity and accuracy is slightly greater than flame photometric detectors.

Various tape samplers can also be used to monitor H_2S at ambient levels. These operate by passing a measured flow of air across a strip of lead acetate tape. Hydrogen sulfide reacts with the lead acetate to produce lead sulfide which darkens the tape. An optional device measures the degree of darkening which is then related to a pre-calibrated standard to determine the concentration of hydrogen sulfide represented. Sensitivity of this technique is approximatly equal to the previous two but it has a slightly lower accuracy. Problems that may occur with tape samplers derive from variations in the air flow rate, temperature fluctuations, sensitivity to temperature and in homogeneities in the tape itself.

A fourth method of measuring hydrogen sulfide concentrations is through cards coated with lead acetate and exposed to air for a given length of time. The duration of exposure is governed by the expected concentrations to be measured. The relative darkness of the exposed cards are compared to standards printed around its perimeter to determine average concentration for a given exposure time.

Monitoring standards may also specify detailed quality assurance criteria including calibration routines, precision and accuracy check techniques, reporting requirements and siting criteria. In addition, monitoring standards may require measurement of meteorological data, back-up techniques, emission quantities and rates.

Hydrogen Sulfide Levels in Hawaii

Prior to the Hawaii geothermal project in Puna, there was little interest in measuring hydrogen sulfide concentrations in ambient air. Since that time, some data have become available though nothing approaching an accurate characterization of background hydrogen sulfide for the Puna region has yet been attempted. Because the ambient H₂S levels are affected by natural volcanic and fumarolic activity, an adequate study must include estimates of the rate and nature of hydrogen sulfide emissions from these sources.

A summary of reported ambient concentrations of hydrogen sulfide is given here.

<u>Location and Period</u>	<u>H₂S in ppm</u>
Sulfur Bank (5/76-8/81)	7.4
Halemaumau (6/76-8/78)	1.2
Kilauea (1971 fissure 8/78)	.03
Puhimau (12/76-8/80)	.03
HGP-A (1978)	
Well Head	20.0
Property Line	.06
Kahaualea (Campbell Estate)	less than .03 (detection limit)

Early measurements at HGP-A prior to installation of the generating facility (1975-1976) were reported simply as less than .2 ppm. This may reflect limitations of their instrumentation rather than values approaching .2 ppm.

Mercury

Mercury, (chemical element symbol Hg) in its elemental form is a silvery, odorless liquid metal at room temperature. Mercury is a commercially important metal used in the manufacture of electrical apparatus, electrolytic preparation of chlorine and caustic soda, antifouling paints and mildewcides, pharmaceuticals, dental work and herbicides and pesticides. It appears as elemental and organic and inorganic compounds. In terms of geothermal facilities and their impact on humans, the most important of these is elemental mercury vapor and mercuric chloride ($HgCl_2$), the most common forms deriving from such facilities.

Concerns about mercury's health effects stems from its affinity in the body for sulfur and sulfhydryl groups in membranes and enzymes. Exposure to mercury can affect membrane structure and function and enzyme activity. The exact toxicological effects of elemental mercury and its various compounds each differ depending, among other factors, on their stability in an organism, route of entry and dose.

Localized exposure to mercury may irritate the skin and mucous membranes. Systemic effects from exposure to high concentrations of mercury vapors focus primarily on the lungs and may cause interstitial pneumonitis and bronchitis, coughing and chest pain. Exposures to lower levels over long periods of time may produce widely varying symptoms in different individuals, including fatigue, anorexia, weight loss, tremors, insomnia and gastrointestinal distress. Chronic exposure to inorganic mercury produces four major symptoms: gingivitis (inflammation of the gums), irritability, muscular tremors and excessive salivation.

The most frequent exposure to mercury occurs in the occupational environment -- mainly mining and the chlor-alkali industries. Occupational exposures as high as 5 mg/m^3 have been recorded in mining operations.

Volcanic regions are known to have higher ambient mercury concentrations than other areas. Measurements taken at various locations relative to Kalalua on the island of Hawaii confirm that elevated atmospheric levels of mercury occur during eruptions. To what degree this reflects

dispersion of mercury emitted from the eruption versus increased fumarolic emissions is useless for some sites. However measurements taken at the HGP-A well site after it had been shut down (20 Km EWE for the Kalalua vent) suggest that dispersion did account for at least part of the elevated levels recorded. These elevated ambient levels are significant in that they represent sustained exposures to plants and animals.

Even during non-eruption phases total mercury levels at fumaroles are very high (5-80 mg/m³). Ambient levels of 1 mg/m³ in the Puna region in general are common.

Mercury deposition in soils and its presence in plant tissues may be measured to provide baseline data for future comparisons and to assess the level of the element (and derivative compounds) in the ecosystem. Presently, little empirical data on the effects of geothermal emissions on plant and soil mercury levels is available, though mercury's effects at higher concentrations as a toxicant are clear.

There are no national or local ambient standards for mercury though the Environmental Protection Agency has suggested a 30 day average of 1 mg/m³. Others have recommended ambient standards for mercury ranging from .1 to 10 mg/m³.

The Hawaii Department of Labor, Division of Occupational Safety and Health set the following standards as a Threshold Limit Values-8 hour time weighted averages:

Alkyl Mercury Compounds	.01 mg/m ³
Other forms	.05 mg/m ³

The National Institute of Occupational Safety and Health recommends a .05 mg/m³ 8 hour time weighted average.

The American Conference of Governmental and Industrial Hygienists had adopted a TLV-TWA of .05 mg/m³ and has set a tentative short term exposure limit of .15 mg/m³.

TABLE 4
PAST AMBIENT MERCURY DATA AT HGP-A AND OTHER SITES
ISLAND OF HAWAII
(Concentrations in mg/m^3)

DATE	SULFUR BANKS	HALEMAUMAU KAU	HGP- PUNA	HILO
April 1971	22.6	-	-	-
May 1971	20.5	-	-	0.31
August 1971	40.7	40.5	-	-
January 1972	2.2	0.7	-	-
April 1972	33.5	-	-	-
December 1973	0.9	-	-	-
May 1975	2.6	-	1.1	0.44
May 1976	5.3-10.0	-	1.2	-
June 1976	47.5	5.0	0.9	-
July 1977	1.4	3.9	0.8	0.8
February 1978	9.6	-	1.57	0.6
August 1978	20.4	4.2	0.9	-
November 1979	6.0	-	1.06	0.8

(From Siegel, S.M. and B.Z. Siegel, The Impact of Geothermal Resource Development in Hawaii (Including Air and Water Quality), Hawaii Energy Resource Overviews, 1980.)

TABLE 5
MERCURY LEVELS OUTSIDE THE HGP-PUNA DRILL SITE AREA:
COMPARATIVE AIR AND WATER DATA, 1971-1976

SAMPLE	Hg CONTENT
Air	<u>ug/m³</u>
Thermal	
Hawaii	0.7-40.7
Iceland	1.3-37.0
U.S.S.R.	0.3-18
Kamchatka-Kuriles	
Non-thermal	
Hawaii	0.04-0.3
Iceland	0.62-1.0
New York	0.014
Cincinnati	0.03-0.21
Eastern Pacific (open sea-west of California)	0.0007

(From Siegel, S.M. and B.Z. Siegel, The Impact of Geothermal Resource Development in Hawaii (Including Air and Water Quality), Hawaii Energy Resource Overviews, 1980.)

While it is known that mercury levels are higher in areas of volcanic activity than in other areas, it is not clear what long term health effects these levels represent. In addition insufficient data exists to define baseline levels for the Puna area that take into consideration the contribution of natural sources, their variability and their dispersion patterns. Until such data are available, only very tentative conclusions can be drawn regarding the impact of geothermal development on atmospheric mercury.

Radon

Radon (chemical element symbol Rn, atomic number 86) is a noble radioactive element that occurs naturally in gaseous form throughout the earth. The most stable form of the isotope is ^{222}Rn , a product of the alpha disintegration of $^{226}\text{Radium}$. Two other isotopes of radon commonly occur: ^{219}Rn - produced by the alpha disintegration of $^{223}\text{Radium}$ and a member of the actinium series; and ^{220}Rn of the thorium series produced by the disintegration of $^{224}\text{Radium}$. Radon generally refers to ^{222}Rn , its most stable form, with a half-life of 3.82 days. ^{220}Rn is sometimes referred to as actinon and ^{219}Rn as thoron.

The presence of radon in geothermal emissions is of concern due to the effects of ionizing radiation on human tissues. Radon decays to form various daughter products and the result of the decay is the emission of highly energetic particles. In the case of the disintegration of ^{222}Rn , an alpha particle is emitted. These particles consist of two protons -- the nucleus of the helium atom. Ultimately these particles acquire two electrons and become an atom of the element helium. These relatively high energy particles interact with biological tissues disrupting the chemical bonds composing those tissues and resulting in chemical substances and interactions alien to the affected organism. If sufficient radiation of this nature is absorbed by human tissues, various ill effects may occur include carcinogenesis and chromosomal damage. In the course of their interaction with biological tissue alpha particles lose energy and can travel only a finite distance. On average (distances traveled vary with the initial energy of the particles and the tissues involved) an alpha particle may travel 30 to 40 micrometers in human tissue (3 or 4 cell diameters).

Units of measurement of "radioactivity" take various forms:

Curie: the curie is a measure of disintegration historically derived from the disintegration of $^{226}\text{Radium}$. The curie is now defined as the quantity of a radio nuclide which is decaying at the rate of 3.7×10^{10} (37 billion) disintegrations per second.

This measure is frequently expressed as smaller fractions of a curie: nano curies (nCi) being one billionth (10^{-9}) of a curie or 37 disintegrations per second; and pico curies (pCi) being one trillionth (10^{-12}) of a curie or .037 disintegrations per second.

Rad: a rad is a measure of dosage (expressed for a specific biological tissue of interest) measured in ergs (a unit of energy measure) per gram. Though independent of time, rads are frequently expressed in terms of a specified period such as microrads per hour. One rad is equivalent to 100 ergs of energy delivered to one gram of tissue. It should be noted that because of differential tissue responses to various forms of radiation, rads should be evaluated in terms of the body parts receiving the dose.

Rem: since various types of radiation affects individual tissues differentially, a measure was devised which relates the relative biological effectiveness of a particular type of radiation to the dose received. The rem is defined in terms of equivalences. One such equivalence defined by O.S.H.A. is that one rem is equal to a dose of one rad due to X, gamma or beta radiation.

Because the major product of biological concern from ^{222}Rn is alpha particles, radiation sources exterior to a human body would not affect internal organs since alpha particles would be stopped within a few cell diameters in the human epidermis. If alpha particles gain access to internal organs however, they can constitute a potential carcinogen. Radon for example may be inhaled and some of it and its daughter products may be deposited on the mucous covered epithelial lining of the respiratory tract. Measurement of how much of the alpha particles emitted actually reach the cells of the sensitive bronchii (the two main branches of the trachea that lead to the lungs) is extremely difficult to measure (estimates vary by a factor of 200).

Because radon is a gas, virtually all of it that is inhaled is exhaled immediately (except for a small quantity that goes into the blood via fatty tissue). Radon however, is accompanied by its particulate daughters (decay products including $^{218}_{84}\text{Polonium}$ and $^{214}_{84}\text{Polonium}$ [half lives of 3.05 minutes and 2.73 minutes respectively]) which may be retained in the respiratory mucosa. Of importance here is the extent to which these daughters reach the bronchii and their role in inducing lung cancer.

Alpha particles are of primary interest here because the effect of radon and its daughters is on a very thin layer of epithelial cells in the bronchii. Since alpha particles expend virtually all their energy in this layer they are of overwhelming importance relative to gamma and beta emissions.

Because of the extreme difficulty of estimating rad and rem measures for the interactions described above, yet another measure was developed to deal specifically with radon and its daughters. This is the working level (WL) which refers to any combination of radon daughters which, during decay to $^{210}_{82}\text{Pb}$ emit a total of 1.3×10^5 MeV of alpha particle energy. This corresponds to the concentration of radon daughters that yield the same amount of alpha particle energy as the radon daughter products in equilibrium with radon at a concentration of 100 pCi/liter. This measure was developed for use in measuring exposure of miners to radon in uranium mines and most data available regarding radon exposure is expressed in working levels. None of the available data on geothermal emissions in Hawaii has been expressed in these units probably because ambient levels of radon are so low relative to mine exposures.

The United Nations Scientific Committee on the effects of atomic radiation estimates that the radon concentrations worldwide over land average about .1 pCi/liter of air. Over sea these may be as low as .001 pCi/liter air.

Representative levels of radon activity in various geothermal areas are:

<u>Location</u>	<u>Fluid Type</u>	<u>Radon (pCi/l air)</u>
Tuila & Kirchurich Volcanoes, Kamchatka	Fumarole gas	5-11
North Island, New Zealand	Fumarole gas	370-340,000
Geyers, California	Well gas	8,770-31,400
Salton Sea, California	Well steam	3,800
Surtsey Volcano, Iceland	Fumarole gas	520-171

<u>Location</u>	<u>Fluid Type</u>	<u>Radon (pCi/l air)</u>
Larderello, Italy	Well gas	200-68,460
HGP-A well, Puna Hawaii	Steam	760-2,400
HGP-A facility perimeter	Ambient	.009

In response to problems with radon emissions from building materials, the Environmental Protection Agency suggested a guideline of habitable structures of .5 pCi/liter of air.

The State Department of Health specifies limits as follows:

30 pCi/liter of air -- 40 hours week

10 pCi/liter of air -- 168 hours week

If HGP-A data is characteristic of other reservoirs in the area, it is unlikely that radon contamination of ambient air would occur as the result of geothermal emissions.

Sulfur Dioxide

Sulfur dioxide (SO_2) is a colorless, non-flammable gas at room temperature with a strong suffocating odor. Various sulfur oxides (SO_x) have been of great concern as atmospheric pollutants because they are one of the primary emissions associated with fossil fuel power generation. Untreated coal and petroleum fuels and natural gas all yield sulfur oxides in varying amounts depending on the quantity of sulfur in the fuel. Many communities therefore regulate the amount of sulfur that coal and petroleum used in power plants can contain. Sulfur dioxide is naturally emitted from fumaroles and active volcanoes.

There has been extensive research on the effects of SO_2 on plants due to the prevalence of SO_2 as a pollutant in industrialized countries. Such pollution has resulted in economically important crop injuries as well as damage to ornamental vegetation and forests. Symptoms of SO_2 poisoning of plants occur most visibly as leaf markings -- the nature and extent of which are highly variable from species to species. Because similar leaf markings may be due to a variety of other causes, such data must be interpreted very cautiously. In addition, there may exist a synergistic effect on plants as a result of the presence of sulfur dioxide together with ozone and nitrogen dioxide. Plant sensitivity to sulfur dioxide also varies as a result of maturity and humidity.

In Hawaii, plants that have colonized volcanic regions may represent resistant species since natural SO_2 levels in such areas are higher than for cleaner environments elsewhere. The specific effect of sulfur dioxide on these plants may be different than those which have been studied elsewhere.

The localized effects of sulfur dioxides on humans at normally encountered levels include irritation to the mucous membranes of the upper respiratory tract, rhinitis, coughing and dryness of the throat. Systemic effects vary from fatigue and bronchitis to asphyxia in high concentrations.

The Environmental Protection Agency has developed national primary and secondary standards for sulfur oxides as follows.

National Primary

80 ug/m³ (.03 ppm)
Annual arithmetic mean
365 ug/m³ (14 ppm)
Maximum 24 hour average not
to be exceeded once per year

National Secondary

1300 ug/m³ (.5 ppm)
maximum three hour average
not to be exceeded once per
year

The State Department of Health has established the following ambient standard:

Annual arithmetic mean	20 ug/m ³ (.008 ppm)
24 Hour arithmetic mean	80 ug/m ³ (.03 ppm)

California ambient air standards for SO₂:

24 Hour mean	110 ug/m ³ (.042 ppm)
1 Hour maximum	1300 ug/m ³ (.5 ppm)

Occupational exposure limits are as follows:

O.S.H.A.	8 hours	TWA	13 ug/m ³ (5 ppm)
Hawaii Division of O.S.H.	8 hours	TLV-TWA	1 mg/m ³ (.04 ppm)
	5 minutes	STEL	3 mg/m ³ (.12 ppm)
N.I.O.S.H. (recommended)	8 hours	TWA	1.3 mg/m ³ (.5 ppm)
A.C.G.I.H.		TLV-TWA	5 mg/m ³ (2 ppm)
		STEL	10 mg/m ³ (5 ppm)

Elevated levels of sulfur dioxide are known to occur as a consequence of volcanic and fumarolic emissions. Representative levels of such emissions are:

Sulfur Bank, mean (5/76-8/81)	21 mg/m ³ (8 ppm)
Kilauea Main Vent, mean (6/76-8/78)	12 mg/m ³ (4.7 ppm)
Kilauea 1971 fissure (8/78)	55 mg/m ³ (21.2 ppm)
Puhimau, mean (12/76-8/80)	.13 mg/m ³ (.05 ppm)

Insufficient data are available to predict the degree to which sulfur dioxide emissions from geothermal facilities may pose an environmental hazard. It did not appear to constitute such a problem at HGP-A.

Carbon Dioxide

Carbon dioxide (CO₂) is a colorless, odorless, inflammable gas. It acts as a simple asphyxiant. At concentrations of 1.5% (15,000 ppm) it may cause some changes in physiological processes at prolonged exposures. At concentrations of 5% (50,000 ppm) it may cause headaches and shortness of breath. At concentrations of 10% (100,000 ppm) it may produce unconsciousness and death.

<u>O.S.H.A. Standards</u>		
8 hour TWA	5,000 ppm	9,000 mg/m ³

<u>A.C.G.I.H.</u>		
8 hour TLV-TWA	5,000 ppm	9,000 mg/m ³
STEL	15,000 ppm	18,000 mg/m ³

There is no State or National ambient standard for CO₂.

Though locally elevated levels of CO₂ can be found at active vents and fumaroles, it is unlikely that CO₂ levels could be increased by geothermal development to the point where they pose a health hazard.

Carbon Monoxide

Carbon monoxide (CO_2) is a clear, odorless, flammable gas. Its toxic effects stem from its affinity for blood hemoglobin (over 300 times that of oxygen). In sufficient concentrations it can reduce the ability of the blood to distribute oxygen to body tissues resulting in death. Symptoms at lower concentrations include headache, dizziness, nausea and collapse.

Standards

O.S.H.A.	8 hours TWA	55 mg/m^3	50 ppm
N.I.O.S.H.			
(recommended)	8 hours TWA	38.5 mg/m^3	35 ppm
N.I.O.S.H.			
(recommended)	Ceiling	220 mg/m^3	200 ppm
Hawaii Division			
of O.S.H.	8 hours TWA	55 mg/m^3	50 ppm

Federal Primary and Secondary Ambient

8 hour average	10 mg/m^3 (9 ppm)	not to be exceeded more than once per year
1 hour average	40 mg/m^3 (37 ppm)	not to be exceeded more than once per year

Hawaii Ambient Standards

8 hour average	5 mg/m^3 (4.5 ppm)
1 hour average	10 mg/m^3 (9 ppm)

Though locally elevated levels of CO may occur as a result of volcanic and fumarolic emissions they still fall short of constituting a health hazard. Examples include:

Sulfur Bank, mean (5/76-8/80)	1.9 ppm
Kilauea Main Vent, mean (6/76-8/78)	.5 ppm
Kilauea 1971 fissure (8/78)	1.2 ppm
Puhimau, mean (8/80)	1.2 ppm

It is highly unlikely that geothermal development will pose a significant threat to air quality in terms of carbon monoxide.

Other Substances

Though other gases may be present in geothermal emissions, only those discussed previously are of immediate significance. It is important to realize however that this is based on the information of HGP-A -- a single well tapping a single reservoir for a short period of time. It is possible that the chemistry of geothermal fluids will vary with time at a single well and between wells. The probability and the extent to which this might occur remain undetermined.

In light of this, two other toxic substances of concern should be considered as potential emissions, though HGP-A data show they weren't of importance there. Both arsenic and boron are known to occur in geothermal fluids. In the Geysers region of California, boron is second only to hydrogen sulfide as an emission of concern. Arsenic (and arsine AsH_3) is a possible pollutant known in some areas but was not significant at HGP-A.

Particulates do not appear to be a potential pollutant associated with geothermal development. Well drilling, testing and Clean-out does release particulates in the air and blowouts have the potential to. Such releases would probably be short lived and minimal. Silicon dioxide (SiO_2) particulates precipitated from waste liquids should be easily and inexpensively controllable.

Because of the high rainfall in the Puna area, several atmospheric emissions may be "scrubbed" from the air by precipitation. These include hydrogen sulfide, mercury, radon daughters, sulfur oxides (yielding from SO_3 sulfuric acid - H_2SO_4) and possibly arsenic and boron. Because rain catchment systems provide potable water for many area residents the possible consequences of such contamination should be assessed for each facility. At HGP-A this did not pose a problem.

WATER QUALITY

In the process of utilizing geothermal fluids to generate energy, large volumes of waste liquids result. These may contain dissolved and suspended substances which for various reasons may pose an environmental hazard. These liquids are normally disposed of by percolation into the group or reinjection into the geothermal reservoir. Because ground waters have characteristically low flow velocities, once contaminated they tend to remain so for very long periods, hence it is important to assess the potential import of such disposal on local aquifers.

On the island of Hawaii the hydrology within the region of current geothermal development is still poorly understood. Because no surface streams traverse the area and marine disposal of waste fluids is highly improbable, this discussion will focus on potential groundwater effects of geothermal development.

The steps involved in evaluating the environmental consequences of disposal of waste liquids in the ground include:

Define the subsurface hydrology

- *are aquifers present in the waste release area?
- *do they contain water that can be withdrawn and used?
- *what are the relationships between these aquifers (vertical and horizontal flow velocities, between them)?
- *are there chemical constituents in the subsurface geological strata which could be leached out by the liquids disposed and be redeposited in the aquifers defined?

What are the chemical constituents of the fluid to be disposed of?

- *specify nature, toxicity volume and concentration of each
- *define likely interaction of such constituents -- are they likely to act synergistically to produce a deleterious effect on the environment?

Determine if such releases will significantly contaminate groundwater

- *will the released liquid reach that aquifer?
- *if it does will it be diluted and rendered harmless or will it have an adverse affect?

Geothermal facilities have a number of possible release points where liquid wastes may enter the ground. These include the well casing, pumps, valves and pipes subject to failure and release of fluids, settlement and percolation ponds, and reinjection wells. The flow rates for the substances under consideration at each of these points must then be specified and the effect of each potential release defined. Given sufficient data various modeling techniques can then be used to predict approximately the movement of the released fluids.

Evaluation of these factors must be made on a site-by-site basis. Though the chemistry of the fluids may be similar between wells, the subterranean hydrology is unlikely to be.

At HGP-A, for example, the geothermal reservoir is believed to have only minimal hydraulic communication with the sea and none with adjacent groundwater tapped by water wells. No detectable affect of the well emissions was noted in rooftop rainwater samples at several nearby residences.

A possible avenue of groundwater contamination that conceivably could occur is associated with disposal of drilling muds. Certain mud formulations occasionally contain toxic substances. The disposal of these should be monitored. If such mud additives are used, their disposal should be monitored.

A list of E.P.A. standards for substances associated with geothermal facilities that may affect water quality in the area is given in Table 6.

TABLE 6
EPA DRINKING WATER QUALITY STANDARDS

<u>Constituents</u>	<u>Maximum Level*</u>
<u>Primary Standards</u>	
Inorganic Chemicals	
Arsenic	0.05
Barium	1
Cadmium	0.010
Chromium	0.05
Lead	0.05
Mercury	0.002
Nitrate (as N)	10
Selenium	0.01
Silver	0.05
 Gross Alpha Particle Activity	 15 PCi/l
<u>Secondary Standards</u>	
Chloride	250
Copper	1
H ₂ S	0.05
Iron	0.3
Manganese	0.05
pH	6.5-8.5
Sulphate	250
Total dissolved solids	500
Zinc	5

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